

MARKED UP VERSION OF THE SUBSTITUTE SPECIFICATION

NEGATIVE ELECTRODE ACTIVE MATERIAL FOR USE IN ALKALINE CELL
AND METHOD OF PREPARING THE SAME

BACKGROUND OF THE INVENTION

The present invention relates to negative electrode active materials for use in
5 alkaline cells and, ^M more particularly, ^{the present invention concerns} to a negative electrode active material for use in
a cell which ^{has a} is low ~~in~~ gas generation and which is prepared by mixing ^{trivalent} a metal whose
~~valence number of trivalence as its oxide~~ is chemically stable at room temperature
and atmospheric pressure with an alloyed zinc powder including zinc as a main
component, and a method of preparing the same. ~~The term "a metal whose valence~~
10 ~~number of trivalence as its oxide is chemically stable at room temperature and~~
~~atmospheric pressure" herein used means a metal whose trivalent compound such as~~
~~an oxide thereof is chemically stable at room temperature and atmospheric pressure.~~

Zinc has been favorably used as a negative electrode active material since it
has ^{a suitable} an appropriate potential when used as a negative electrode for a cell in an
15 aqueous solution system, as well as it is low-priced. However, ~~its corrosion potential~~
~~is more base than the decomposition potential of water so that~~, when it contacts an
electrolytic solution, zinc corrosion and decomposition of water occur to generate a
hydrogen gas. Such hydrogen gas generation not only reduces ^{the} cell capacity of zinc as
a negative electrode material, but also, when used in a closed-type cell, increases an
20 inner pressure of the cell to bring about leakage of the electrolytic solution therefrom
and, in a worst case, ^{two} burst of the cell.

Heretofore, hydrogen generation has been controlled by alloying zinc, surface
^{treating} treatment of zinc particles, adopting a suitable composition of electrolytic solution
and addition of a corrosion inhibitor to the electrolytic solution. In other words, ~~at~~ ^{for}
25 alloying zinc, a zinc alloy including some components selected from the group

which
is
an
oxide
thereof

consisting of Al, Bi, In, Ga, Sn, Pb and the like has primarily been used in a manner that a ~~composition~~ ratio of these elements ^{to zinc} is optimized relative to gas generation.

However, ~~it is a present situation that~~ such optimization ratio is not ~~enough to solve~~ ^{sufficient} ~~the problems.~~

5 Moreover, although a method of adding an indium compound such as indium oxide, indium hydroxide or the like, or a bismuth compound such as bismuth oxide, bismuth hydroxide or the like to an electrolyte gel has been proposed, this method is hardly expected to provide ~~a stable effect~~ ^{stable results} and, in addition, it necessitates to mix a zinc powder and an additive in the electrolyte gel at the same time, ~~whereupon~~ ^{mixing} ~~work of solid and liquid is troublesome.~~ ^{which results in}

SUMMARY OF THE INVENTION

As described above, alloying zinc and other methods have been performed so as to control hydrogen gas generation; however, it is hard to say that any of them can ~~provide~~ ^{achieve} ~~obtain a fully stable effect.~~ Accordingly, the object of the present invention is to

15 provide a negative electrode active material for use in a cell which will reduce hydrogen gas generation from zinc to be brought about when it contacts an electrolytic solution and a method of producing the same.

The present inventor has conducted intensive studies in order to solve the aforementioned problems of the prior art and has found that the addition of a ^{trivalent} ~~metal~~ ^M ~~having trivalence~~ to an alloyed zinc powder by the dry mixing method, ~~in more~~ particularly, the addition of a metallic powder of either Bi or In to the conventional alloyed zinc powder for use in a cell by the dry mixing method, preferably in a range of 50 - 1000 (ppm) based on the weight of the alloyed zinc powder, can substantially improve the characteristics of the mixed product which is a powder for use in a

25 cell showing low hydrogen gas generation; ~~hence, the~~ ^{The} present invention has been

the present inventor discovered

accomplished on the basis of ^{these} findings.

In accordance with one aspect of the present invention, there is provided a negative electrode active material for use in an alkaline cell comprising a composition composed by mixing a ^{trivalent} metal, ~~whose valence number of trivalence~~ is ^{which is an oxide thereof} 5 chemically stable ~~as an oxide thereof~~ at room temperature and atmospheric pressure, with a zinc alloy powder for use in a cell.

In accordance with another aspect of the present invention, there is provided a negative electrode active material for use in an alkaline cell comprising a composition composed by mixing a ^{trivalent} metal, ~~whose valence number of trivalence~~ as ^{which is} 10 oxide thereof is chemically stable at room temperature and atmospheric pressure with a zinc alloy powder for use in a cell by 50 to 1000 ppm based on the weight of the zinc alloy powder for use in the cell.

In accordance with another aspect of the present invention, there is provided the negative electrode active material for use in the alkaline cell as described above, in which the ^{afore said trivalent} metal ~~whose valence number of trivalence as the oxide thereof is~~ 15 ~~chemically stable at the aforementioned room temperature and the aforementioned atmospheric pressure~~ is Bi or In.

In accordance with another aspect of the present invention, there is provided the negative electrode active material for use in the alkaline cell as described above, 20 in which the metal is a metallic powder with an average particle size of 100 μ m or less.

In accordance with another aspect of the present invention, there is provided a negative electrode active material for use in an alkaline cell of low gas generation comprising mixing the metallic powder ^{with} ~~to~~ a zinc alloy powder for use in a cell under 25 a dry condition.

In accordance with another aspect of the present invention, there is provided a method of preparing a negative electrode active material for use in an alkaline cell comprising a composition composed by mixing a ^{trivalent} metal, ~~whose valence number of trivalence~~ is chemically stable as an oxide thereof at room temperature and atmospheric pressure, to a zinc alloy powder for use in a cell.

which as an oxide present
In accordance with another aspect of the present invention, there is provided a method of preparing a negative electrode active material for use in an alkaline cell comprising the step of mixing a ^{trivalent} metal, ~~whose valence number of trivalence~~ as an oxide thereof is chemically stable at room temperature and atmospheric pressure, to a zinc alloy powder for use in a cell by 50 to 1000 ppm based on the weight of the zinc alloy powder for use in the cell.

In accordance with another aspect of the present invention, there is provided the method of preparing the negative electrode active material for use in the alkaline cell as described above, in which the ^{trivalent} metal ~~whose valence number of trivalence as the oxide thereof is chemically stable at the aforementioned room temperature and under the aforementioned atmospheric pressure~~ is Bi or In.

In accordance with another aspect of the present invention, there is provided the method of preparing the negative electrode active material for use in the alkaline cell as described above, in which the aforementioned metal is a metallic powder with an average particle size of 100 μ m or less.

In accordance with another aspect of the present invention, there is provided a method of preparing a negative electrode active material for use in an alkaline cell ^{having} of low gas generation comprising the step of mixing the aforementioned metallic powder ^{with} to a zinc alloy powder for use in a cell under a dry condition.

25 BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph in an embodiment of the present invention showing a relationship between the amount of metallic Bi powder added to the alloyed zinc powder and gas generation amounts; ~~and~~

Fig. 2 is a graph in an embodiment of the present invention showing a relationship between the amount of metallic In powder and the gas generation amount.

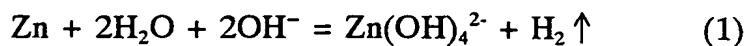
DETAILED DESCRIPTION OF THE INVENTION

The ^{mixed} trivalent metal-~~mixed~~ zinc powder according to the present invention can easily be prepared by mixing a trivalent metal powder (with a particle size of under 100 μ m) such as a powder of Bi, In or the like with a conventional alloyed zinc powder under a dry condition. The product thus obtained is readily available as a zinc powder for use in a cell which is low in hydrogen gas generation.

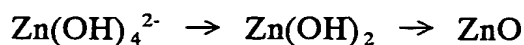
In other words, by mixing of these metallic powders, a negative electrode active material with extremely low hydrogen gas generation, which has never been achieved by the ^{conventional} alloying method, can be obtained. Moreover, by employing the thus prepared ^{mixed} trivalent metal-~~mixed~~ zinc powder as a negative electrode material for use in an alkaline cell, an alkaline cell which ^{has desirable} ~~is excellent in~~ preservability, storability and safety can be provided.

^{The} Mechanism of controlling hydrogen gas generation by mixing the trivalent metallic powders ^{with} ~~to~~ the zinc powders has not been resolved, but is considered to be as follows:

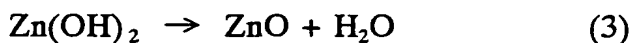
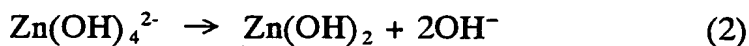
Generally, the reaction of hydrogen gas generation is considered as follows:



$\text{Zn}(\text{OH})_4^{2-}$ ion produced in the above formula (1) undergoes further reaction with an increase in its concentration as follows:



Namely,



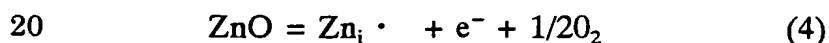
5 The thus produced coating has a construction of Zn/ZnO/Zn(OH)₂/Zn(OH)₄²⁻ in ^{the} order from the side of electrolytic solution toward the side of zinc.

Since a Zn(OH)₂ coating is of a porous sediment, ZnO basically plays an important role as an anti-corrosive coating. In fact, it is considered that a very thin ZnO coating is formed when zinc contacts the electrolytic solution and, accordingly,
10 a gas generation reaction shown in formula (1) advances by the reaction of Zn which has moved through the ZnO coating to the surface of the electrolytic solution even if zinc is not exposed to the electrolytic solution at a possible crack in the coating.

ZnO is a nonstoichiometric compound of excess Zn type illustrated by Zn_{i+δ}O in which excess amount of Zn exists as interstitial ions.

15 The more the amount of interstitial ions, the more the amount of Zn which moves through the ZnO coating to the surface of electrolytic solution and, accordingly, the higher the gas generation shown in formula (1).

An interstitial zinc ion, i.e., Zn_i · , is formed by a reaction shown in the following formula:



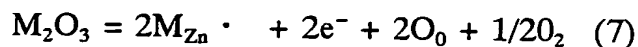
in which equilibrium constant (K) is shown as follows:

$$K = [\text{Zn}_i \cdot] \cdot [e^-] \cdot P_{\text{O}_2}^{1/2} \quad (5)$$

It is considered that P_{O₂} is constant in this case so that formula (5) can be restated as follows:

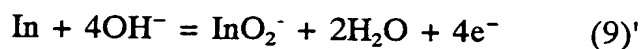
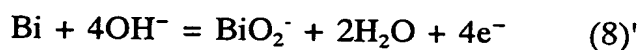
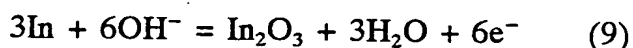
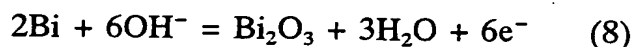
$$25 \quad K_i' = [\text{Zn}_i \cdot] \cdot [e^-]$$

If a portion of ^{the} Zn site of ZnO is substituted with a trivalent ion, i.e., M^{3+} ~~at~~
~~this point~~, ^{the} following formula can be obtained:



Since electrons, i.e., e^- , are supplied according to formula (7), the reaction
 5 shown in formula (4) advances leftward whereupon the amount of interstitial Zn ions,
 namely, $Zn_i \cdot$, is decreased. Ion species which moves ^{or} in the coating is ~~this~~
 interstitial Zn ion^s, $Zn_i \cdot$, so that the decrease of the amount of $Zn_i \cdot$ leads to the
 decrease of the amount of Zn which moves up to the surface of the electrolytic
 solution, thereby resulting in controlling ^{the} zinc corrosion reaction (which is equal to ~~the~~
 10 hydrogen gas generation reaction) shown in formula (1).

Bi and In shown in the present invention become respective trivalent oxides
 or ions in a high-alkaline electrolytic solution in accordance with the following
 reactions and then the thus produced ionized chemical species of these dissolve in the
 ZnO coating to make respective solid solutions through substitutions (reference: M.
 15 Pourbaix: "Atlas of Electrochemical Equilibria in Aqueous Solutions" NACE (1974)):



20 Since electrons, e^- , are supplied according to formula (7), electrical
 conductivity of an oxidized coating is increased.

When trivalent ions of metals such as Bi, In and the like are taken into the
 ZnO coating during the ZnO forming step in which the electrolytic solution and zinc
 contact each other, hydrogen gas generation will be reduced to increase ^{the} electrical
 25 conductivity of the coating.

In order to produce a Bi or In solid solution effectively in the ZnO forming step, it is necessary for a suitable amount of the powder of one of these metals to be effectively dispersed on the surfaces of zinc particles.

To attain this, it is necessary for an average particle size of the ^{additional} mixed metal to be 100 μ m or less and, moreover, its addition is preferably within a range of 50 to 1000 (ppm) based on the weight of zinc alloy powder for use in a cell. If the addition is less than 50 ppm, an ^{advantageous result of such} ~~effect to be brought about by the~~ addition will not ~~appear~~ ^{occur}. Whereas if the addition is over 1000 ppm, ^{the} cell capacity will decrease, ^{and} ~~as well as an~~ ^{advantageous result of such} ~~effect to be brought about by the~~ addition increment will not ~~appear~~ ^{occur}.

10 Examples and Comparative Examples are provided below for the purpose of further illustrating the present invention, but are in no way ^{are} to be taken as limiting ~~it~~ ^{the} ~~present invention~~. Also ~~and also~~ the alloyed zinc powder composition and the mixed metal powders according to the present invention are by no means limited to ^{that} ~~being employed in the~~ illustrated ^{in the} Examples and Comparative Examples. Unless otherwise stated, all parts and percentages are herein given by weight.

Comparative Example 1

Alloyed zinc powders with a composition composed of Bi of 89 ppm, Al of 31.1 ppm, In of 516 and the rest of Zn and with particle sizes of 75 to 850 μ m were prepared by the atomizing method.

20 A 40% KOH electrolytic solution saturated with zinc oxide was added to the thus prepared alloyed zinc powders and kept at 60°C. On the basis of gas generation of the third day, a gas generation amount was calculated (in a unit of μ l/g \cdot day). Gas generation measurements ^{where} ~~have been~~ performed on five pieces of the above-prepared sample. As a result, an average of 18.32 (μ l/g \cdot day) and a standard deviation of 1.586 (μ l/g \cdot day) were obtained.

Example 1

50 ppm, 100 ppm, 300 ppm, 500 ppm and 1000 ppm of the bismuth powder available from Saitama Dowa High-Tech Co. was respectively mixed, based on the weight of the alloyed zinc powder described in Comparative Example 1, with the alloyed zinc powder described in Comparative Example 1 to prepare samples (No. 1 to No. 5) which were then ^{subjected to} ~~put on~~ the gas generation tests in the same way as in Comparative Example 1. Test results are shown in Table 1. The results are also shown in a graph in Fig. 1.

From the test results, it has been confirmed that mixing of metallic bismuth is effective in controlling gas generation and, particularly, a mixing amount of 500 (ppm) or more is effective for decreasing the gas generation.

Table 1

	(μl/g · day)				
	Addition Amounts of Metallic Bi Powder (ppm)				
	50	100	300	500	1000
No. 1	16.52	16.34	14.61	9.99	10.31
No. 2	14.37	14.80	14.49	7.73	4.67
No. 3	17.53	15.81	14.73	8.21	8.90
No. 4	15.38	15.02	15.90	9.34	11.94
No. 5	14.50	14.3	11.07	6.93	9.77
Average	15.66	15.25	14.16	8.44	9.12
Standard Deviation	1.353	0.815	1.817	1.230	2.722

Comparative Example 2

Alloyed zinc powder with a composition composed of Bi of 89 ppm, Al of 32.8 ppm, In of 520 and the rest of Zn and with a particle size in the range of 75 to 850 μm was prepared by the atomizing method.

A 40% KOH electrolytic solution saturated with zinc oxide was added to the thus prepared alloyed zinc powder and kept at 60°C. On the basis of gas generation of the third day, a gas generation amount was calculated (in a unit of μl/g · day).

Gas generation measurements ^{were} ~~have been~~ performed on five pieces of the above-prepared sample in the same way as in Comparative Example 1. As a result, an average of 23.53 ($\mu\text{l/g} \cdot \text{day}$) and a standard deviation of 1.682 ($\mu\text{l/g} \cdot \text{day}$) were obtained.

5 Example 2

50 ppm, 100 ppm, 300 ppm, 500 ppm and 1000 ppm each of metallic indium (with purity of 99% or more and particle sizes of less than $100\mu\text{m}$) available from Kojundo Kagaku Kenkyusho was mixed, based on the weight of the alloyed zinc powder described in Comparative Example 2, with the alloyed zinc powders
10 described in Comparative Example 2 to prepare respective samples (No.1 to No.5) which were then subjected to the gas generation tests in the same way as in Comparative Example 2. Test results are shown in Table 2. The results are also shown in a graph in Fig. 2.

From the test results, it has been confirmed that mixing of metallic indium is
15 effective in controlling gas generation since the gas generation was gradually decreased with an increase of metallic indium mixing in each sample.

Table 2

	$(\mu\text{l/g} \cdot \text{day})$				
	Addition Amounts of Metallic In Powder (ppm)				
	50	100	300	500	1000
No. 1	22.67	20.00	22.67	19.33	21.33
No. 2	22.00	22.67	21.33	22.87	18.82
No. 3	22.00	22.72	18.00	20.00	20.33
No. 4	22.00	22.67	23.33	20.09	20.67
No. 5	22.45	20.01	19.45	20.03	19.21
Average	22.22	21.61	20.96	20.46	20.07
Standard Deviation	0.335	1.344	2.372	1.569	1.063

As has been described above, the negative electrode active material for use in
20 the alkaline cell according to the present invention is easily obtained by mixing a

- powder of trivalent metal such as Bi, In or the like with the conventional alloyed zinc powder under a dry condition. The product thus obtained is a zinc powder for use in the cell which shows low hydrogen gas generation, having attained reduction of gas generation to such an extent that it has never been attained by the conventional
- 5 alloying method and, moreover, the powder is capable of providing an alkaline cell which ^{how desirable} ~~is excellent in~~ preservability, storability and safety.